DIARYL KETONE PEROXIDES

BY

VELMA E. NICHOLS

B.A., University of Oklahoma, 1928

M.S., University of Oklahoma, 1932

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
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ACKNOWLEDGMENT

The author is indebted to Professor C. S. Marvel for the direction and criticism of this work.

Introduction

A diaryl ketone peroxide $(Ar_2CO_2)_2$ was isolated in this laboratory from the ozonization of a 1,1-diaryl-1-alkene. Since such a compound had not been reported in the literature it has been the object of this research to investigate the generality and mechanism of the formation of diaryl ketone peroxides through the ozonolysis of olefins, to synthesize them by other methods, and to study their properties.

Experimental and Discussion of Results

Through the ozonolysis of the corresponding 1,1-diarylethenes benzophenone, *p*-tolyl ketone, *m*-toyl ketone, *p*-tolyl phenyl ketone and *p,p'*-dichlorobenzophenone peroxides were synthesized in 3-7 per cent yields and characterized. Benzophenone peroxide was obtained also from the ozonolysis of 1,1-diphenyl-1-propene, 1,1-diphenyl-1-butene, triphenylethene and tetraphenylethene (from the latter compound in 57 per cent yield calculated on the basis of $(C_6H_5)_2C{=}CR_2$). An insufficient quantity of *o*-tolyl ketone peroxide was obtained for analysis and 3,5-dimethyphenyl ketone peroxide could not be separated from the ketone although its presence was indicated by melting behavior. Along with the peroxides, as aromatic products, were obtained small amounts of the aromatic acids, derived from oxidation of one of the aryl nuclei, and the aromatic ketones, which formed the major products of the reactions. The peroxides were separated from the ketones by solution of the latter compounds in alcohol, ether or acetone.

In these reactions both crude ozone and ozone which had been washed by passing through dilute aqueous sodium hydroxide and concentrated sulfuric acid prior to introduction into the reaction mixtures were used. Benzophenone peroxide was isolated from ozonolysis mixtures which were yet strongly unsaturated toward bromine in carbon tetrachloride. Various solvents and temperatures varying from $-60°$ to room temperature were used without affecting greatly the yield of peroxide. The method of decomposition of the ozonolysis mixture, e.g., anhydrous, with water, with water and hydrogen peroxide, with dilute alkali, or treatment with phosphorus pentoxide before decomposition, did not seem to be a factor in determining the quantity of peroxide formed.

Small amounts of benzophenone and *p*-tolyl ketone peroxides were

obtained by allowing the respective ketones to stand in solution or suspension with aqueous and dry ethereal extractions of 30 per cent hydrogen peroxide for several months. Benzophenone peroxide was isolated also from reaction mixtures of benzophenone dichloride and aqueous and ethereal solutions of hydrogen peroxide. It could not be isolated from mixtures of the ketone and Caro's acid, a method which had been used for the preparation of aliphatic ketone peroxides but which had failed to give alkyl aryl ketone peroxides[1]. Neither could the peroxide be obtained from the action of ozone on benzophenone.

All of the ketone peroxides melted sharply in the neighborhood of 200° with some liberation of oxygen and formation of the corresponding ketones. Molecular weight determinations, ebullioscopically in benzene or cryoscopically in camphor, indicated them to be dimeric. Although difficultly soluble in all solvents they could be recrystallized from benzene, acetone and ethyl acetate. They resemble acetophenone peroxide[1] in their stability, inertness, non-explosibility and non-oxidizing properties.

A small amount of benzoyl peroxide was obtained from the ozonization of benzaldehyde. This peroxide has not been reported by other investigators of this reaction[2].

The known dimeric benzaldehyde peroxide $(C_6H_5CHO_2)_2$[1] was isolated for the first time from ozonolysis mixtures of styrene, stilbene and triphenylethene.

An effort was made to determine whether a hydrolytic decomposition[1] or simple cleavage of the ozonide was involved in the formation of the alkylidene peroxides. Di-hydroxybenzal peroxide $(C_6H_5CHOHO)_2$[1] could not be isolated from the decomposition of ozonolysis mixtures from either stilbene or styrene. The aqueous decomposition of di-hydroxybenzal peroxide, prepared by the addition of hydrogen peroxide to benzaldehyde, gave no benzaldehyde peroxide. On the other hand, benzaldehyde peroxide was obtained from the anhydrous decomposition of styrene ozonolysis mixtures prepared over anhydrous copper sulfate. Moreover, similar types of products and quantities of peroxides were observed from anhydrous and aqueous decompositions of ozonolysis mixtures from both 1,1-diarylethenes and 1-arylethenes. These results indicate that aldehyde and ketone alkylidene peroxides are formed through simple cleavage of the ozonide molecules and not through a hydrolytic mechanism involving the intermediary of di-hydroxyalkyl peroxides.

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VITA

The author was born May 7, 1909, in Caddo County, Oklahoma, where she received her elementary and high school training. She was awarded the degree of Bachelor of Arts by the University of Oklahoma in 1928 and that of Master of Science in 1932. During the years 1929-1931 she held a graduate assistantship in chemistry at the University of Oklahoma and from 1933 to 1935 she was an instructor in chemistry and mathematics in the junior college at Poteau, Oklahoma. In September 1935 she began graduate work in chemistry at the University of Illinois.

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